PATENT SPECIFICATION

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(54) MULTIPLE PANES

(71) We, SAINT-GOBAIN INDUSTRIES, a Body Corporate organised under the laws of the French Republic, of 62 Boulevard Victor Hugo, 92209 Neuilly Sur Seine, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a fire resistant multiple pane formed of at least two parallel spaced glass sheets, a gel occupying the space between the sheets.

Such panes originally were developed for forming port holes or walls of glove boxes used in the nuclear industry.

Water being essentially transparent and forming, on the one hand a good protection against fire because of its high heat of vaporisation, and having on the other hand an excellent neutron section, initially airtight panes were made formed of two or more glass sheets spaced one from the other, the space thus defined being filled with water.

However, in the case of accident, shock or fire, the water may flow away instantly and protection against neutrons, or against propagation of flames in the case of fire resistant panes, is no longer ensured.

To eliminate the risk of loss there has been proposed panes in which the space between the glass sheets is occupied by a filling of an aqueous gel. Such transparent gels which are used, among other things, for stabilizing earth (see for example French Patent 1,458,945), are formed by a polymer which is present in the form of a network of microcavities, which may be closed or unclosed containing a liquid generally water.

This network of closed microcavities stops the gel flowing and the liquid which it contains from flowing away: in the case of shock entailing breakage of the glass sheets the gel thus continues to play its role, both against propagation of fire and as a neutron screen, to the extent that water to be vaporised remains in the microcavities of the matrix and giving an increased time in which security services can take action. However for thicknesses compatible with the requirements of weight and cost of panes of large dimensions the fire resistance is not sufficient to fulfil the requirements of fire security standards which are required for fireproof partitions in buildings.

DIN Standard 4102, for example, defines a method of testing and the criteria to which panes for buildings have to conform to be classified in the "fire resistant" category.

Materials tested according to this standard are classified by the time during which, under standard trial conditions, they remain capable of performing the following functions:

— sufficient mechanical strength for the element considered to continue to carry out its function,
— thermal insulation,
— resistance to flames,
— absence of the emission of inflammable gas from the surface exposed to heat during the trial (special trial for reaction to fire).

The thermal insulation is considered satisfactory when the mean heating of the non-exposed face (mean of the temperatures recorded on the non-exposed face) and the maximum heating (maximum temperature indicated by the least favourable, thermo-

couple arranged on the non-exposed face) do not exceed respectively 140 and 180° C.

The "fireproof" elements are those for which all the criteria mentioned above are met.

In each category the classification expresses in degrees, as a function of the time during which the elements satisfy the trials, the degree of retention of the above-mentioned properties: the "degree" is the average time equal to or immediately less than the durations during which the element has met the properties required.

For applications to buildings there are desired panes which have fireproof characteristics for at least thirty minutes without having to use exaggerated thicknesses.

Known panes comprising aqueous gels between two sheets of glass cannot pretend to fulfill the requirements reliably for fire proof conditions for thirty minutes or more, unless they have large thicknesses which make them incompatible with construction requirements.

It is, on the other hand, known to make fire proof panes by placing between two sheets of glass a solid layer of a product which under the action of heat radiation is transformed into an insulating foam, for example a hydrated alkaline silicate. Such panes are described in French Patent No. 2,027,646. Their optical properties and in particular their transparency leave something to be desired; further they are not fireproof for thirty minutes except when using certain methods of construction in which, for example, the layer of silicate is reinforced with glass fibres or several separate panes which are mounted in the same frame in order to form a multiple pane which makes the optical quality even more mediocre.

According to the present invention, there is provided a fire-resistant pane which comprises at least two parallel glass sheets separated by a space filled with a gel, the gel comprising from 65 to 95% by weight of a liquid having a high heat of vaporisation and from 1 to 20% by weight of a substance compatible with the gel capable of forming a heat-insulating foam under the effect of thermal radiation. The gel may advantageously be based on a derivative of acrylic acid, the liquid having a high heat of vaporisation may be water and the substance capable of giving a foam may be a soluble salt chosen from the group formed by aluminates, silicates, stannates, plumbates, alums, borates, phosphates and other salts of an alkali metal or ammonium.

In one embodiment the gel comprises an acrylamide and the metal salt is a soluble silicate.

Other advantages and characteristics of the invention will appear from the description which follows.

The structure of the fireproof pane according to the invention may be of a known type and so will not be described in detail. It may also be of the type described in our co-pending British Patent Application No. 1,294,177 (Serial No. 1,541,372).

The description which follows is therefore limited to the composition of the gel interposed between two parallel glass sheets of a multiple pane. This gel essentially comprises two constituents, that is:

— a solution of gelifiable fireproofing product,
— a solution of a soluble mineral salt compatible with the preceding solution and capable of forming a foam under the action of thermal radiation.

The gelifiable solution may comprise derivatives of acrylic acid mixed in equal amounts, for example, methylolacrylamide and acrylamide, which can polymerise in aqueous solution. The polymerisation of these products may be carried out using peroxides or persalts with the addition of an accelerator, for example diethylaminopropionitrile (DEAPN), and possibly a cross-linking agent such as N,N′-methylenebisacrylamide (NN′—MBA).

Table I below gives different gel compositions by way of example.

TABLE I

Components	% by weight					
Acrylamide Rocagil 1295 (Registered Trade Mark)	10	15	25	35	45	50
10% by weight aqueous ammonium persulphate solution.	5	5	5	5	5	5
DEAPN	0,4	0,4	0,4	0,4	0,4	0,4
Water	84,6	79,6	69,6	59.6	49,6	44,6

The stability of the gels prepared with a cross-linking agent is superior, that is to say the more heavily cross-linked gel gives less shrinkage and better adhesion to glass sheets.

Table II below gives various compositions of gel with variable contents of the reticulating agent N—N' MBA.

TABLE II

Components	% by weight			
Acrylamide Rocagil 1295	20	20	20	20
10% by weight aqueous ammonium persulphate solution.	4	4	4	4
DEAPN	0,3	0,3	0,3	0,3
N—N' MBA	0,0	0,2	0,3	0,4
Water	75,7	75,5	75,4	75,3

The Applicant has found that the cohesion of the gels increases with their content of acrylamide. Also, their cohesion increases with increased cross-linking, and hence with an increasing percentage of reticulating agent.

It is believed that the high content of water in these substances gives them good fireproofing properties.

Thus, when there is subjected to flame a pane formed of two parallel glass sheets separated by a space filled with this gel, it is found that the glass sheet exposed to fire breaks rapidly but then the layer of gel forms a screen which prevents the heat spreading and reaching the second sheet of glass during a time which, other things being equal, is a function of the thickness of the gel layer.

In fact, during a large part of the time when the gel contains water and this water evaporates regularly the temperature of the gel remains close to 100° C.

When a large proportion of the water has evaporated, if the gel is used on its own the organic matrix which forms the microcavities is destroyed, disintegrates and allows passage of heat radiation which very rapidly reaches the second sheet of glass causing its destruction.

By addition to the gel of a substance capable of forming an insulating foam under the effect of heat radiation, the period of evaporation of water contained in the microcavities is prolonged such that the moment when the gel is consumed and no longer plays the part of a screen is retarded.

Thus it is possible to prepare gels which contain increasing percentages of soluble metal salts, for example 5 to 20% by weight of sodium silicate in 30% aqueous solution (see Table III below).

TABLE III

Components	% by weight					
Sodium silicate in 30% aqueous solution	5	8	10	12	15	20
Rocagil 1295	20	20	20	20	20	20
10% persulphate	4	4	4	4	4	4
DEAPN	0,3	0,3	0,3	0,3	0,3	0,3
N–N′ MBA	0,3	0,3	0,3	0,3	0,3	0,3
Water	q.s. 100	q.s. 100	q.s. 100	q.s. 100	q.s. 100	q.s. 100

Beyond 10% by weight of silicate in 30% aqueous solution, i.e. beyond 3% by weight of silicate as such, the gel becomes opalescent but still has useful optical characteristics, in particular a transmission power which exceeds 60%.

Examples of multiple panes according to the invention and their fire-resisting properties are given below.

There are made three double panes of dimensions 410×410 mm, formed of a glass sheet of 6mm thickness reinforced with metal wires and a tempered glass sheet also of 6 mm thickness, the two sheets being spaced by 24 mm.

In the space between the sheets, there are introduced respectively one of the compositions A, B and C given in Table IV below.

TABLE IV

	Compositions (% by weight)		
	A	B	C
Acrylamide, Rocagil 1295	25	12,5	12,5
Ammonium persulphate	4	4	4
DEAPN	0,3	0,3	0,3
N–N′ MBA	0,3	0,3	0,3
Sodium silicate	0,0	3	4,5
Water	70,4	79,9	78,4

These panes are subjected to a fire resistance test, according to DIN 4102, the reinforced face being turned towards the fire. Five thermocouples being fixed onto the tempered glass to measure the increase in temperature at different points, the following results are obtained:

Sample A (24 mm thickness of transparent gel without silicate):

— 1 minute 30 secs. :	Breakage of reinforced glass.
— 3 minutes:	The gel becomes unstuck from the reinforced glass in the centre.
— 8 minutes:	The gel becomes brown in the centre, the gel is attacked. Formation of bubbles which break.
— 23 minutes:	The gel is three quarters opaque. Fairly irregular attack in small zones. Continual bubbling, vapour towards the interior of the furnace.
— 30 minutes:	Unsticking of the gel from the tempered glass. Appearance of water. Uniform temperature of tempered glass: 55° C.
— 33 minutes:	The gel bulges. Flowing water is seen. Intense bubbling.
— 35 minutes:	Hole in the gel, at the top.
— 36 minutes:	Breakdown of the gel which has remained clear in the mass.
— 37 minutes:	The two upper thermocouples reach 160° C., (whereas the ambient temperature is 20° C.). End of test.

It is seen that this sample acted as a fire breaker for 30 minutes, and it is only after 37 minutes that the tempered glass reached 160° C. The safety margin of 7 minutes is not however sufficient to ensure completely the characteristics required for a "30 minute fire break".

Sample B (24 mm thickness of gel and 3% silicate):

— 1 minute 30 secs. :	Breakage of the reinforced glass sheet.
— 6 minutes:	The gel shows surface cracks on the fire side.
— 8 minutes:	The reinforced glass bulges.
— 12 minutes:	Start of release of uninflammable vapours at the periphery of the pane.
— 17 minutes:	A large amount of smoke, but non-inflammable.
— 20 minutes:	Regular attack of the gel, good behaviour of the reinforced glass, which is not broken up.
— 28 minutes:	The smoke diminishes.
— 35 minutes:	Stop of smoke.
— 45 minutes:	The gel is attacked in the centre and becomes hollow.
— 52 minutes:	Hole in the gel. The central thermocouple reaches 160° C. the same temperature as that positioned above. End of test.

It is seen that with 3% sodium silicate the fire break duration is brought to 52 minutes.

Sample C (24 mm thickness of gel at 4.5% of silicate):

— 2 minutes:	Breakage of reinforced glass.
— 7 minutes:	Gel becomes unstuck from reinforced glass.
— 8 minutes:	Reinforced glass bulges.
— 13 minutes:	Release of uninflammable smoke towards the exterior.
— 16 minutes:	Stop of release of smoke. Gel becomes opaque.
— 21 minutes:	Fresh discharge of smoke.
— 29 minutes:	A lot of smoke generated, still uninflammable.
— 33 minutes:	Total opacity of pane.
— 36 minutes:	Stop of discharge of smoke.
— 40 minutes:	Reinforced glass starts to flow but remains in place.
— 46 minutes:	The glass becomes thinner at the upper part of the pane on the side exposed to the fire.
— 50 minutes:	Tearing of the gel at the level of the frame, at the upper part.
— 54 minutes:	Breakage of tempered glass. End of trial.

No thermocouple had reached at this moment 160° C.

The end of the trial was not owing to increase of the temperature to 160° C. on the tempered glass, but due to breakage of this glass due to the temperature gradient which it was subjected to. It is believed that this sample mounted in an improved

frame such as that described in the above-mentioned patent specification No. 12944/77 (Serial No. 1,541,372) would be a firebreak for more than 54 minutes.

Table V below allows comparison of the results, also of the luminous transmissions.

TABLE V

Sample	Fire-break time	Luminous transmission at 555 mn
A (24 mm without silicate	37 minutes	78%
B (24 mm – 3% silicate)	52 minutes	63%
C (24 mm – 4.5% silicate)	54 minutes	25% (estimated)

It is seen that the addition to the gel of 3% of silicate as such allows an increase in the firebreak duration of about 25 minutes, bringing it over the desired 30 minutes by a large margin, whereas the luminous transmission is conserved at 63%.

In the above description and in the Examples above, there has been described a gel to which sodium silicate is added. The silicate may be replaced by the soluble salts such as aluminates, stannates, plumbates, alums, borates, phosphates and other salts of an alkali metal, or ammonium.

The accompanying drawing is a section of a fireproof multiple pane comprising, according to the invention, a spacer layer of gel.

This type of pane has been designed to prolong the resistance of glass to fire, owing to a better distribution of heat between the central zone of the pane and the periphery, which reduces the internal stresses due to thermal gradients.

This pane comprises two glass sheets 1 and 2, held parallel and spaced one from the other by a frame made up of hollow profile members 3. These profile members are adhered laterally to the glass sheets by an internal strip 4 which is watertight, for example of silicone. A second strip 5 is also provided at the edge. The separating space 6 separating the sheets 1 and 2 is filled with a gel according to the invention.

The pane is mounted in a frame made of hollow profile members 7 of rectangular section, by means of two perforated members 8, screwed at 9 and 10 on to the profile member 7. The members 8 each have a part 11, which retains in position a block of glass 12 situated between the sheets 1 and 2 and the members 8.

The member 8 situated on the side exposed to fire, that is to say on the side of sheet 1, is protected from direct thermal radiation by a second frame member 13, with interposition of glass wool 14. A block 15 is interposed between the member 7 and the base of the member 13 and an insulating layer 16 is arranged along the edge of the pane.

When the temperature increases the blocks 12 of glass are softened and are welded to glasses 1 and 2, which, owing to the parts 11 which retain the blocks 12, in place, prevent the sheets from sliding downwardly. In this manner, the gel is maintained for a longer period between the sheets 1 and 2.

WHAT WE CLAIM IS:—

1. A fire-resistant pane which comprises at least two parallel glass sheets separated by a space filled with a gel, the gel comprising from 65 to 95% by weight of a liquid having a high heat of vaporisation and from 1 to 20% by weight of a substance compatible with the gel capable of forming a heat-insulating foam under the effect of thermal radiation.

2. A pane according to Claim 1, in which the gel comprises at least one acrylic acid derivative, said liquid is water and the substance capable of producing a foam comprising a soluble salt chosen from the group formed by the aluminates, silicates,

5. A fire-resistant pane according to Claim 1, substantially as hereinbefore described.

stannates, plumbates, alums, borates, phosphates and other salts of an alkali metal or ammonium.

3. A pane according to Claim 1, in which the gel comprises at least one acrylamide and the substance capable of producing a foam comprises a silicate.

4. A pane according to any one of Claims 1 to 3, in that the glass sheets are maintained spaced one from the other by profile members having the general shape of a T, the head of the T being adjacent the periphery of the pane and the stem of the T being between the sheets.

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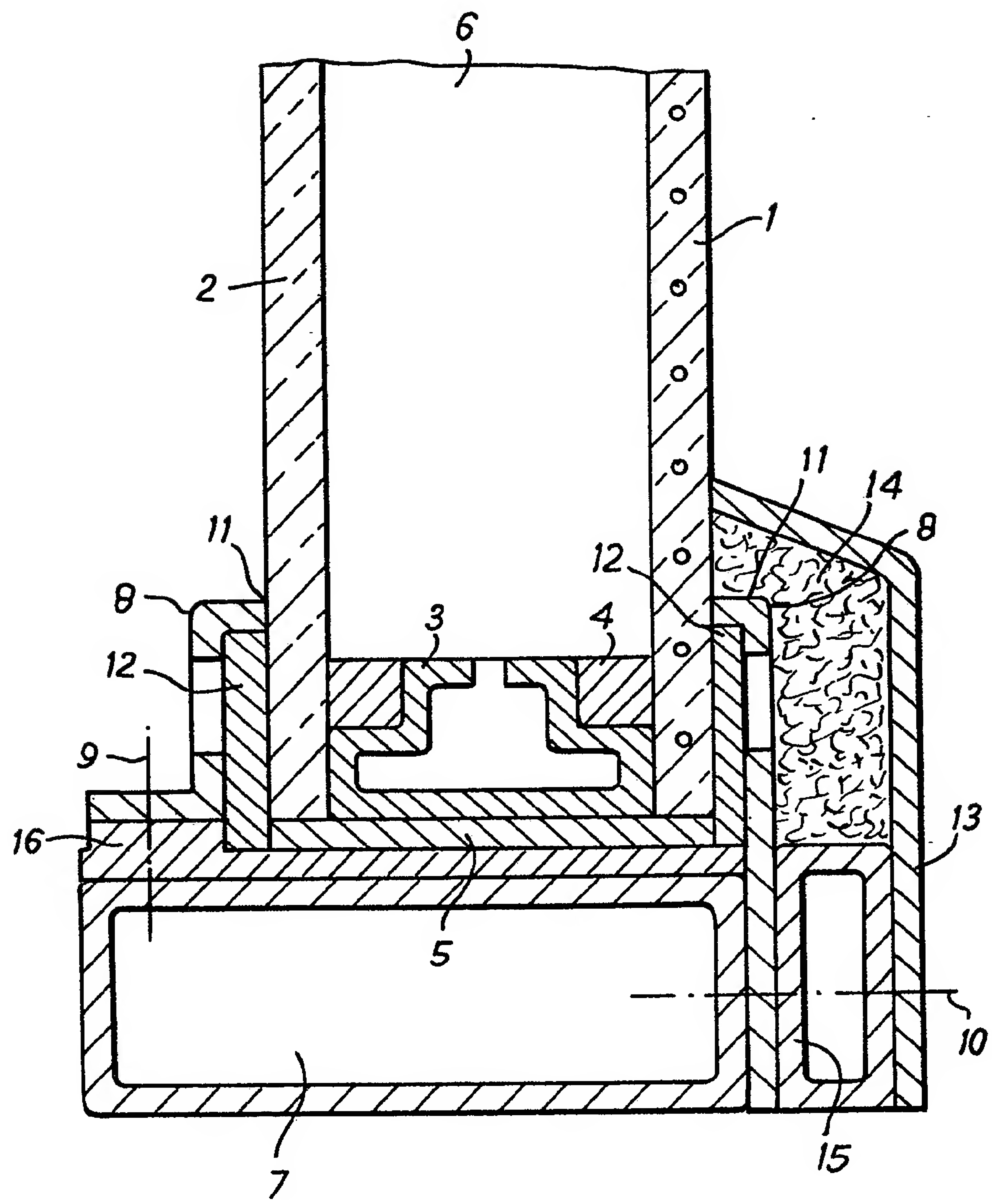
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